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The Durability Characterization of High Temperature Polymer Matrix - Carbon Fiber Composites for Future Air Force Applications

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14. ABSTRACT

Potential critical physical and chemical aging mechanisms in terms of damage initiation and propagation of bismaleimide, BMI and Polyimide, PI, - carbon fiber composites in future aerospace stress-time-temperature-moisture-chemical service environments will be characterized. This characterization will be conducted on the molecular, microscopic and macroscopic structural levels in order to develop structural-performance phase diagrams for mechanics model-structural design analyses and associated materials structural optimization at all dimensional levels.

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## **FINAL REPORT**

### **“The Durability Characterization of High Temperature Polymer Matrix – Carbon Fiber Composites for Future Air Force Applications”**

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## **INTRODUCTION**

### **PROGRAM GOALS**

Characterize the fundamental chemical, physical and mechanical-induced degradation mechanisms that control the critical failure paths of BMI- and PI-C fiber composites, and modify the structure-process-performance relations to minimize or alleviate these failure mechanisms.

### **METHODOLOGY**

Based on our previous durability studies (1) we followed a systematic durability methodology to evaluate the long-term performance of polymers and their composites. This methodology involves initially studying the effects of individual and combined core test service environments upon polymer and composite performance in order to identify the most likely synergistic service environments and controlling physical, chemical and mechanical parameters of the ultimate critical failure path. This methodology requires knowledge of the effects of (i) fabrication and (ii) service environment exposure conditions upon physical and chemical molecular, microscopic and macroscopic structural damage states and how the individual kinetics and synergistic growth of the damage states leads to an unacceptable performance criteria. From this methodology, specific failure path threshold 3-D structural performance phase diagrams are developed that plot three critical parameters that control damage state development, for example, moisture concentration, temperature, molecular physical structural damage state. The information contained in these specific critical phase diagrams can be utilized for:

- Lifetime modeling;
- Structural analyses design optimization;
- Development of meaningful accelerated test procedures; and
- Evaluation of the health of deployed structures.

### **MATERIALS**

The two principal types of high temperature polymer matrix-carbon composite utilized in Air Force applications were studied, namely (i) cross-linked bismaleimide, BMI, thermosets and (ii) predominantly thermo-plastic polyimide, PI, resins and their carbon, C, fiber composites.

### **SUBJECT MATTER AND INVESTIGATORS**

The subject matter of the technical tasks of this program are shown in Table (1), together with the appropriate investigators. Roger J. Morgan was the principle investigator of the overall program.

**TABLE (1) TECHNICAL TASKS AND INVESTIGATORS**

<b>TASK</b>	<b>INVESTIGATORS</b>
<b>(1) BMI COMPOSITE/RESIN STRUCTURE-PROPERTY RELATIONS</b> <ul style="list-style-type: none"> <li>• Cure reaction-network structure</li> <li>• Mechanical Properties vs Temperature</li> <li>• Tg's, density, Moisture Absorption vs Network Structure</li> <li>• Prevention of Cure-Induced Composite Microcracking</li> </ul>	Morgan, Shin, Lincoln (S)
<ul style="list-style-type: none"> <li>• Moisture Absorption Characteristics</li> </ul>	Yee
<ul style="list-style-type: none"> <li>• Fiber-Matrix Interfacial Properties</li> </ul>	Drzal
<ul style="list-style-type: none"> <li>• BMI-Cyanate Ester Blends</li> </ul>	Leung
<b>(2) HYGROTHERMAL INDUCED DAMAGE MECHANISMS OF PI'S AND BMI'S</b> <ul style="list-style-type: none"> <li>• Blister Formation</li> <li>• Thermal Cycling/Spiking</li> <li>• Moisture "Lock-In"</li> </ul>	Shin, Morgan
<b>(3) ACCELERATED SYNERGISTIC TESTING</b>	Shin, Morgan
<b>(4) PI COMPOSITE/RESIN STRUCTURE-PROPERTY RELATIONS</b>	Morgan, Lincoln (S)
<b>* (S) - STUDENT</b>	

## REPORT STRUCTURE

The report structure will follow the task subject matters documented in Table (1). As the major portion of these technical areas are already published, generally each area will consist of a summary with the appropriate literature references.

## REFERENCE

1. R.J. Morgan, "Thermal Characterization of Composites", Chapter 9 in Thermal Characterization of Polymer Materials, (2<sup>nd</sup> Edition), Ed. E.A. Turi, Academic Press, Inc., 1997, pp. 2091-2261.

## TECHNICAL RESULTS

- **TASK (1) BMI COMPOSITE AND RESIN STRUCTURE-PROPERTY RELATIONS**
  - **CURE REACTION-NETWORK STRUCTURE**

The BMI thermoset matrix used in high temperature PMFC's is 4,4 - bismaleimidodiphenyl methane (BMPM)/0,0 - diallyl alcohol of bisphenol A (DABPA), Matrimid 5292, Ciba-Geigy. Systematic Fourier transform infrared spectroscopy, FTIR, and differential scanning calorimetry, DSC, studies of the cure reactions of the BMPM/DABPA BMI resin system as a function of chemical composition and temperature-time cure conditions (1-4) revealed:

- (i) The BMPM and DABPA monomers react in the 100-150°C to reversibly form and "ene" adduct, followed by a Diels-Alder slow condensation reaction between maleimide C=C bonds and propenyl C=C bonds, whose product sterically slows significant further reaction in this temperature region.
- (ii) In the 150-200°C temperature region rapid, free radical polymerization of the C=C bonds occurs, together with slow hydroxyl condensation dehydration to form ether linkages, resulting overall in a complex crosslinked network. FTIR studies show all the maleimide and allyl C=C bonds are consumed under standard cure conditions at 250°C after 3 hours. However, it is uncertain if all the more sterically restricted propenyl C=C bonds are consumed under these standard cure conditions, as it is difficult to detect such groups by FTIR. The ether crosslink reaction is only ~50% complete after 9 hours at 250°C. Our recent systematic mass spectroscopy studies have revealed H<sub>2</sub>O evolution concentrations consistent with this dehydration reaction in this temperature range.
- (iii) In the 250-300°C temperature region further cure occurs via slow, glassy-state diffusion controlled dehydration and possibly free radical propenyl C=C bond polymerization. Further cure of BMI's in this temperature region causes a ~0.2% density decrease; ~0.3 wt % loss; 10% modulus and 25-40% ductility loss in the 25-177°C service environment temperature range and ~100°C increase in T<sub>g</sub>.

The primary performance issue for BMI-C fiber composites is that they are not fully cured under standard 250°C cure conditions and could continue to cure over prolonged periods of time in service environment at 177°C resulting in matrix embrittlement. Extrapolation of all available high temperature reaction rate data to the 175-200°C temperature range indicates insignificant further cure and associated BMI embrittlement occurs in the dry, 175-200°C temperature range service environment because of glassy-state diffusion restrictions and decreases in reaction rates of unreacted species at these lower temperatures. Our analyses reveals no change in toughness after 120,000 hours exposure at 175°C and only a 20% decrease at 200°C for the same time period.

## REFERENCES

1. R.J. Morgan, E.E. Shin, B. Rosenberg and A. Jurek, "Characterization of the Cure Reactions of bismaleimide Composite Matrices", *Polymer*, **38**, 639, (1997).
2. R.J. Morgan, E.E. Shin and J. Zhou, "High Temperature Polymer Matrix-Carbon Fiber Composites-Performance Issues and Future Needs", *Proc. of 44<sup>th</sup> International SAMPE Symp.*, Long Beach, CA, May, 1999, pp. 1098-1110.
3. B.A. Rozenberg, G.N. Boiko, R.J. Morgan and E.E. Shin, "The Cure Mechanism of the 4, 4' - (N, N' - Bismaleimide) Diphenylmethane-2, 2' - Diallyl bisphenol A System", *Polymer Science, Ser. A*, **43**, 386, (2001).
4. B.A. Rozenberg, E.A. Dzhavadyan, R.J. Morgan and E.E. Shin, "A Calorimetric Study of the 4, 4' - (N, N' - Bismaleimide) Diphenylmethane- 2, 2' - Diallyl bisphenol A System", *Polymer Science, Ser. A*, **43**, 400, (2001).

## MECHANICAL PROPERTIES VS. TEMPERATURE

The flexural and tensile mechanical properties of BMI resins were systematically studied as a function of composition, cure conditions and test temperature (1). The optimal mechanical properties were found for a BMI resin with a BMPM : DABPA monomer ratio of 1:0.87 that was cured 1 h at 180°C, 2 h at 200°C and 6 h at 250°C that exhibited failure strains in the 5-7.5% range in the 23-177°C test temperature range.

## REFERENCE

1. E.E. Shin, R.J. Morgan, J. Zhou, J. Lincoln, R. Jurek and D.B. Curliss, "Hygrothermal Durability and Thermal Aging Behavior Prediction of High Temperature Polymer Matrix Composites and Their Resins", *Proc. of 12<sup>th</sup> Annual Technical Conference of the American Society for Composites*, 1113, (1997).

## GLASS TRANSITIONS, DENSITY AND MOISTURE ABSORPTION CHARACTERISTICS VS. NETWORK STRUCTURE

The Tg's, density,  $\rho$ , and moisture absorption characteristics of BMI resin were characterized in terms of cure conditions and BMPM : DABPA monomers composition (1-3). The principal findings were:

- The Tg's progressively increased with increasing cure temperature with a resultant final Tg at 350°C.
- The resin density decreased systematically with increasing cure temperature as result of the rearrangement of the ether crosslinks to stiffer aromatic-like crosslinks that result in a lower packing efficiency.
- The more open networks with the lower densities absorbed progressively more moisture as more resin H-bond sites become accessible.

## REFERENCE

1. R.J. Morgan, E.E. Shin, J. Lincoln and J. Zhou, "Polymer Matrix Composites Performance and Materials Development for Future Aero-Space Applications", Proc. of American Society for Composites, College Station, Texas, Sept. 2000, pp., 1061-1072.
2. J.E. Lincoln, R.J. Morgan and E.E. Shin, "Moisture Absorption-Network Structure Correlations in BMPM/DABPA Bismaleimide Composite Matrices", J. of Advanced Materials, 32, 24, (2000).
3. J.E. Lincoln, Ph.D. Thesis, "Structure-Property-Processing Relationships and the Effects of Physical Structure on the Hygrothermal Durability and Mechanical Response of Polyimides", Michigan State University, May, 2001.

## PREVENTION OF CURE-INDUCED COMPOSITE MICROCRACKING

Transverse microcracks are present in carbon fiber/bismaleimide (BMI) cross-ply composite laminates composed of 4, 4' - bismaleimidodiphenylmethane (BMPM)/ 0, 0' - diallyl bisphenol A (DABPA) matrices after standard cure and fabrication conditions, and grow in width upon subsequent postcure. This investigation (1) characterized cure-induced microcracking in terms of the critical fundamental macroscopic, microscopic, and molecular damage mechanisms and thresholds, and a cure cycle modification that prevents microcrack formation under standard processing conditions for  $[0^\circ/90^\circ]_s$  laminates. A unique *in-situ* technique was utilized in which cure of the laminate was performed inside the chamber of an environmental scanning electron microscope (ESEM), allowing for (i) physical observation of microcrack growth and formation mechanisms and (ii) characterization of microcracking onset time-temperature thresholds. The cure cycle modification that prevents microcracking is an extended initial cure time at 177°C prior to higher temperature cure regimes. Effects of this modification was examined through network structure-property-processing interrelationships by way of (i) dynamic mechanical analysis (DMA), (ii) optical and electron microscopy, (iii) differential scanning calorimetry (DSC), and (iv) our previous work on carbon fiber/bismaleimide composites. From the aforementioned analysis it was concluded that an extended initial cure time at 177°C prior to higher temperature cure steps prevents microcracking under standard fabrication postcure conditions for  $[0^\circ/90^\circ]_s$  laminates; no microcracking was observed until an additional postcure of 6 h at 300°C. This microcrack resistance was independent of initial BMPM : DABPA monomer stoichiometry for the two monomer ratios examined and is associated with an improved

fiber-matrix interface and lower composite residual stress, as a result longer lower temperature cure exposure that allows relaxation of the resin cure shrinkage stresses.

## REFERENCE

1. J.E. Lincoln, R.J. Morgan and E.E. Shin, "Fundamental Investigation of Cure-Induced Microcracking in Carbon Fiber/Bismaleimide Cross-Ply Laminates", *Polymer Composites*, 22, 397, (2001).

## MOISTURE ABSORPTION CHARACTERISTICS

### Background

Advanced composites used in aerospace applications are exposed to harsh conditions involving a wide range of temperatures and humidities. The combination of temperature and humidity extremes can damage these composites, causing component failure over time. The understanding of moisture transport and damage initiation mechanisms in matrix resins and composites is essential to the improvement of long-term durability of advanced composites.

The current AFOSR project focuses on the moisture transport and environmental aging in a BMI resin (Cytac 5250-4 RTM) and its carbon fiber composites. The material properties are monitored during environmental aging and the molecular basis of diffusion and hygrothermal aging is studied.

### Results

#### 1. Network evolution during cure in epoxies

In our previous AFOSR project, we quantified the network topology in epoxies in terms of the nanopore content measured by PALS. A correlation between moisture uptake and the nanopore content was established. Since the network structure of a thermoset resin evolves during cure, cure history is expected to affect the moisture uptake. In the current project, we have monitored the network evolution during cure and systematically studied the effect of cure schedule on moisture diffusion.

In DGEBA/DDM and TGMDA/DDS epoxy systems, the specific volume and nanohole volume below  $T_g$  increase with the extent of cure, indicative of the 3-D nature of the network. In a highly crosslinked system, the rigid crosslinks prevent chain segments from close packing and result an "open" 3-D network in the glassy state. When the moisture absorption properties were correlated with different cure schedules, it was found that more complete cure corresponded to higher water uptake. This can be attributed to increases in both polarity and porosity during cure in epoxies. The above results imply that the moisture resistance of a resin may be improved through judicious design of the cure schedule.

#### 2. Moisture transport in BMI neat resin

The focus of the current project is the water absorption and transport behavior of a BMI and its composites. The moisture transport mechanisms in the neat matrix need to be investigated before a full understanding of the composite behavior is possible. Therefore,



moisture transport in the neat BMI resin was first studied. Most resin samples examined are the flash of various composite panels. As the flash has essentially identical thermal history as the composite, it is ideal in the study of composites.

Fig. 1 shows the water uptake behavior of the neat resin at 70°C. All of the flash samples display similar diffusion behaviors. The most important feature of Fig. 1 is the continued increase in uptake over an extended time scale. Although the initial absorption appears to be Fickian, the weight gain does not reach an equilibrium uptake as predicted by Fick's law. Rather, the uptake continues to increase linearly with respect to  $\sqrt{t}$  after the initial diffusion.

This water uptake behavior is consistent with the two-stage diffusion observed in other polymer-absorbent systems. The two-stage model considers the relaxation process during diffusion. Transport in glassy polymers involves both the concentration-gradient-driven Fickian diffusion and the time-dependent relaxation process. Since the relaxation is usually much slower than diffusion in glassy polymers, the uptake often displays a two-stage behavior with a fast initial absorption followed by a slow approach to a final true equilibrium. We have developed a two-stage model to explain the observed moisture uptake behavior in BMI.

By assuming the relaxation is much slower than diffusion, we can treat the first and second stages as diffusion and relaxation controlled, respectively. During the second stage, relaxation is the rate-determining factor and the concentration remains uniform in the material. As the uptake increases linearly as a function of  $\sqrt{t}$  in the second stage as seen in Fig. 1, we propose the saturation concentration to be a linear function of  $\sqrt{t}$ .

$$c_s = c_0 + k\sqrt{t} \quad (1)$$

Then the weight gain in the second stage is given by

$$M = 2hc_s = 2hc_0 + 2hk\sqrt{t} = M_0(1 + k'\sqrt{t}) \quad (2)$$

Since the initial diffusion obeys Fick's law, the uptake in the entire experimental time scale can be approximately written as

$$M_t \cong M_{\infty 0}(1 + k\sqrt{t}) \left[ 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp\left[-(2j+1)^2 \pi^2 \left(\frac{D_x t}{h^2}\right)\right]}{(2j+1)^2} \right] \quad \text{or,} \quad (3)$$

$$M_t \approx M_{\infty 0}(1 + k\sqrt{t})(1 - \exp[-7.3(Dt/h^2)^{0.75}])$$

Curve fit using the current two-stage model (Eq. (3)) is shown in Fig. 1 as the solid line. Very satisfactory fit to the experimental data was achieved. The success of this two-stage model suggests that the network structure relaxes slowly in the presence of water, which is in agreement with the plasticizing effect of water. Water molecules can plasticize the resin and cause segmental rearrangements and swelling. As the network slowly relaxes, more water is absorbed, resulting in the gradual increase in uptake during the second stage.

Desorption and re-absorption experiments were performed to demonstrate the reversibility of the structural relaxation. Fig. 2(a) shows the uptake curves of three consecutive absorption cycles. The re-absorption experiments give consistently higher diffusivity and uptake than the first absorption, which indicates that the structural relaxation is irreversible upon desorption. Moreover, if the time origin is chosen as the start of the first absorption experiment as done in Fig. 2(b), all three absorption cycles exhibit the same slope during the second stage, *i.e.*, same  $k$  value in Eq. (3). If the Fickian diffusion part is ignored for the time being, the data points from the second and third absorption fall onto the same line determined by the first absorption. This important observation implies that the first absorption and re-absorption steps are controlled by the same relaxation process. In other words, the material is in different stages of the same relaxation.

Dynamical Mechanical Analysis (DMA) results further demonstrate the plasticizing effect of water. Fig. 3 depicts the DMA traces of BMI neat resin before and after aging and after an aging-absorption-desorption cycle. Isothermal aging decreases the intensity of the  $\beta$  and  $\gamma$  relaxation peaks, while water absorption at 70°C rejuvenates the aged material and cause the peak intensity to recover. It seems that water can plasticize the material and rejuvenate the aged network. This result supports the moisture-induced relaxation assumption in our diffusion model.

Non-Fickian diffusion in polymers is often caused by chemical degradation such as hydrolysis and oxidation. However, in the current BMI system, substantial chemical reactions due to moisture exposure are unlikely. Our FT-IR experiments show no appreciable change after one absorption-desorption cycle. DMA data after water absorption-desorption indicates the absence of permanent  $T_g$  change, also supporting the lack of significant chemical reactions. The observed non-Fickian diffusion and property change during absorption are more likely caused by physical processes, *e.g.*, structural relaxation.

### 3. Water absorption in composites

Two kinds of carbon fiber reinforcements are used in the composites, woven and uni-weave. The composites studied include woven, uni-weave and hybrid composites. From the data shown in Fig. 4 and 5, one can see that the same two-stage diffusion model can also describe the moisture uptake data in composites. Moisture-induced relaxation seems to be important in the composites as well.

For uni-weave composites, diffusion properties along and across the fiber direction were both measured. Fig. 4 shows the normalized weight gain data of uni-weave 12-ply composite. The normalized composite weight gain is very close to that of the flash, which is consistent with the notion that carbon fiber absorbs little moisture. It also suggests the absence of a strong interface effect on water absorption. As predicted by the mathematical model of diffusion in a two-phase system, diffusivity along the fiber direction is much higher than that across the fiber direction.

Based on the simple geometry of a uni-directional composite,

$$D_{along} = (1 - v_f) D_r; \quad (4)$$

$$D_{across} = (1 - 2\sqrt{v_f/\pi}) D_r$$

$$D_{along} / D_{across} = \frac{(1 - v_f)}{(1 - 2\sqrt{v_f/\pi})} \quad (5)$$

Table 1 shows the diffusivities of uni-weave 12-ply composite at 70°C. The measured  $D_{along}/D_{across}$  ratio is slightly lower than that predicted by Eq. (5) using the fiber volume fraction, indicating the absence of preferred diffusion along the fiber-matrix interface. There does not seem to be substantial debonding between the fiber and the matrix.

At 70°C	D ( $10^{-8} \text{ cm}^2/\text{s}$ )	Edge corrected D	$D_{along}/D_{across}$	Theoretical $D_{along}/D_{across}$
Uni-weave Along fiber	3.3	2.7	2.1	2.5
Uni-weave Across fiber	1.7	1.3		

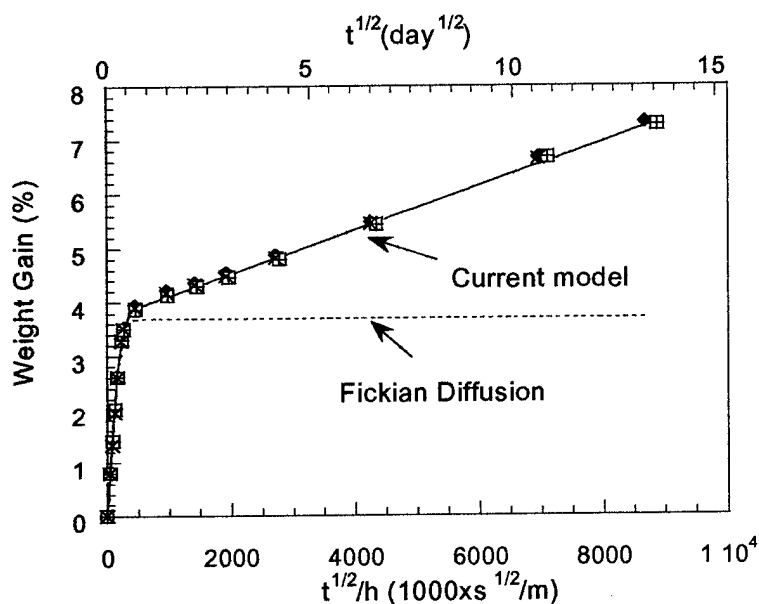
**Table 1. Experimental and theoretical diffusivities of uni-weave 12-ply composite.**

In the case of the woven composite, only diffusion perpendicular to the ply direction was studied. As shown in Fig. 5, the normalized composite weight gain displays a large scatter between specimens. This is probably due to the local fluctuations in fiber fraction in the composite panel. The fiber volume fraction was determined by acid digestion using fairly large composite samples. As the diffusion specimens are rather small, the local fiber content may be quite different from the average value of a much larger panel. The large data scatter in composite weight gain makes the comparison between the composite and neat resin less meaningful in woven composites. However, as seen in Fig. 5, the normalized composite weight gain is generally lower or close to that of the neat resin, suggesting the lack of significant interfacial debonding during water absorption.

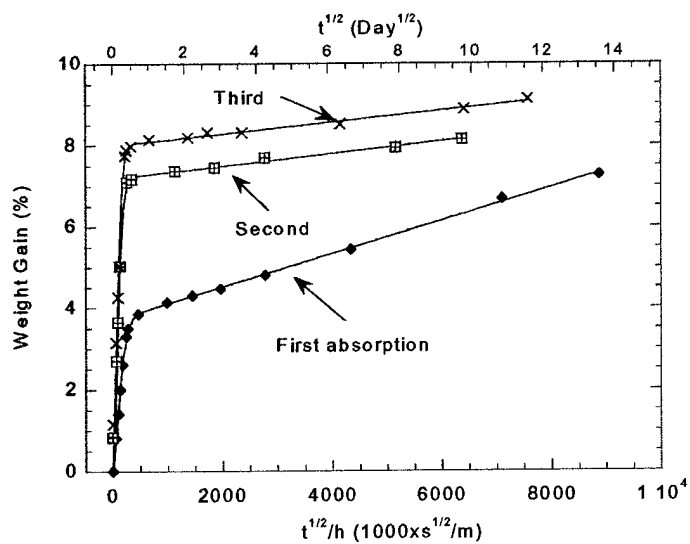
The short-term moisture absorption data discussed above suggest the lack of substantial interfacial damage during absorption. However, hygrothermal damage may develop after prolonged exposure to water. The SEM micrograph in Fig. 6(a) shows the cross section of 3-ply woven composite after one month in liquid water at 70°C. Almost no debonding or cracking was observed, demonstrating good interfacial integrity after short-term exposure. However, after two years in water at 70°C, large cracks developed in the woven composite (Fig. 6(b)). These cracks tend to localize near the resin-rich regions, where the stress due to matrix swelling is the highest. Correspondingly, the composite weight gain shows positive deviation from the current two-stage model after prolonged exposure as shown in Fig. 7. The open cracks can cause additional water uptake in the composites.

## Conclusion

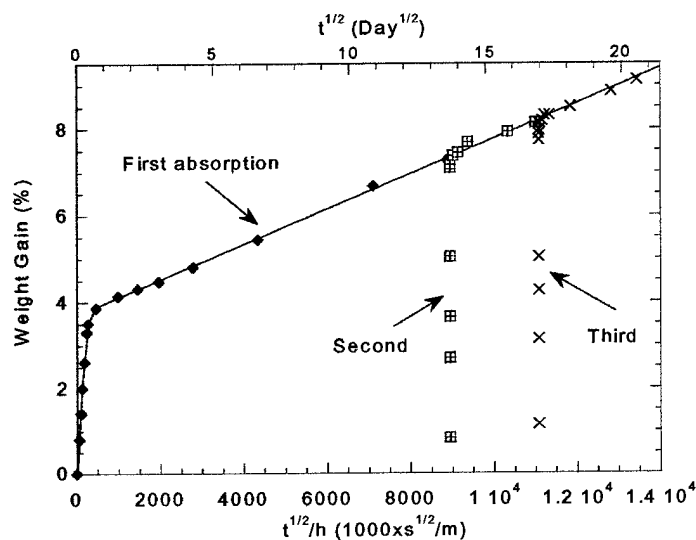
Our research has demonstrated several fundamental aspects of moisture transport and environmental aging in thermosets and composites. First, network topology of a thermoset affects moisture uptake. As the network structure evolves during cure, cure schedule also influences the moisture absorption in cured resins. Secondly, since water can plasticize many thermoset resins, it will induce structural relaxation of the resin. The moisture-induced relaxation causes additional moisture uptake and results in the observed two-stage uptake behavior in BMI. The structural relaxation is irreversible upon desorption, causing higher diffusivity and uptake in the re-absorption experiments. DMA results demonstrate the rejuvenating effect of water. Finally, short-term diffusion data of the composites indicate the lack of substantial interfacial debonding during absorption. However, large interfacial cracks developed near resin-rich regions after prolonged exposure to moisture. These cracks are likely caused by the swelling stress created by absorbed moisture.



**Fig. 1.** The moisture uptake of BMI neat resin at 70°C. The symbols are experimental data and the solid line is the curve fit using the current two-stage model.

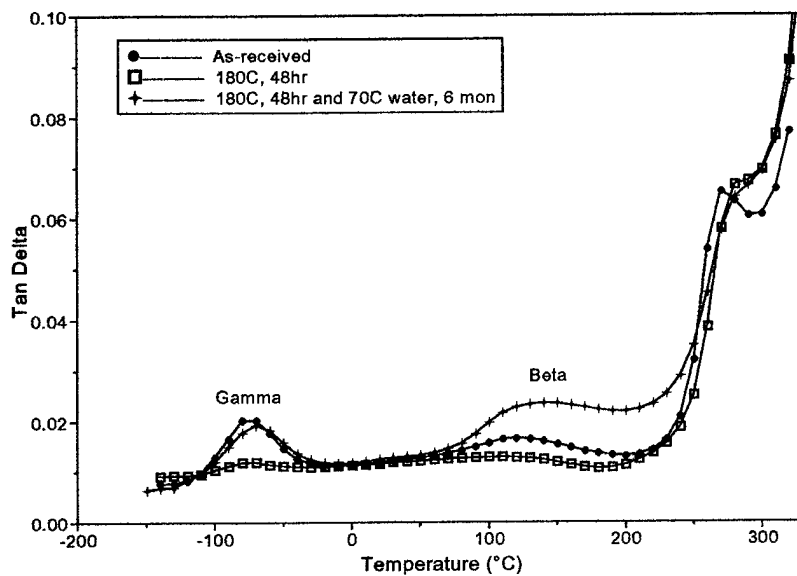


(a)

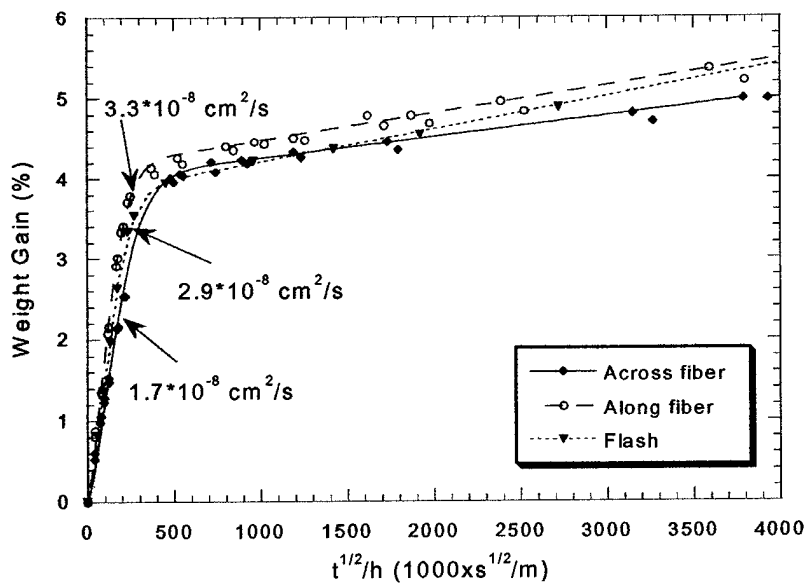


(b)

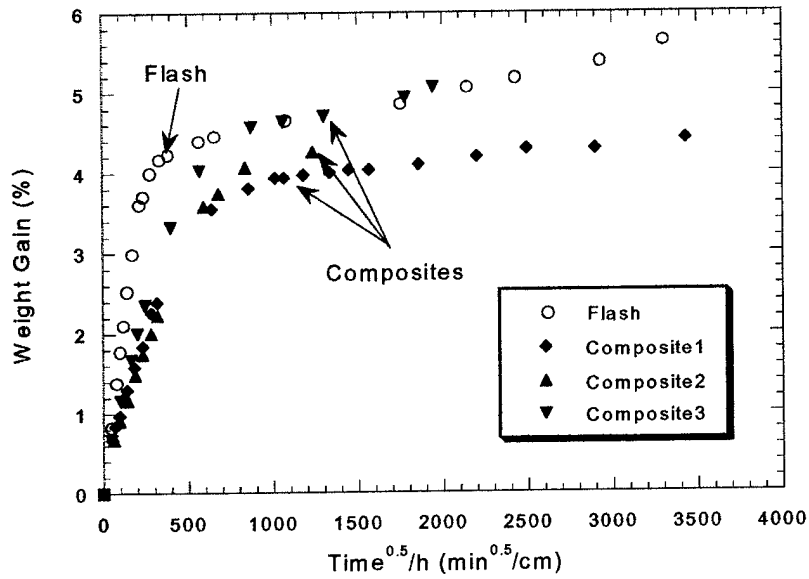
**Fig. 2. Moisture uptake during the first, second and third absorption experiments at 70°C. (a) The elapsed time is counted from the start of each absorption step. (b) The elapsed time is counted from the start of the first absorption experiment. The solid line is the curve fit of the first absorption.**



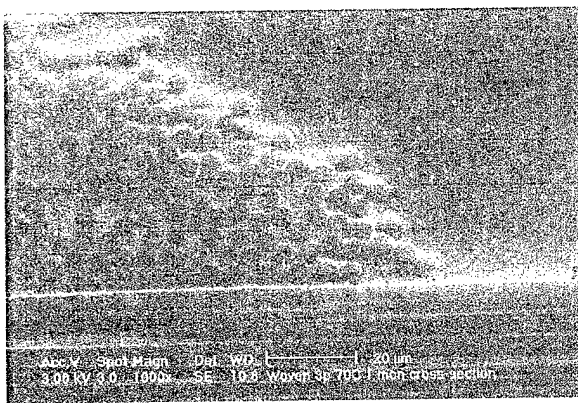
**Fig. 3. DMA traces of BMI neat resin: • as-received, □ after aging at 180°C for 48 hr, + after aging at 180°C for 48 hr, water absorption at 70°C for 6 months and then dried.**



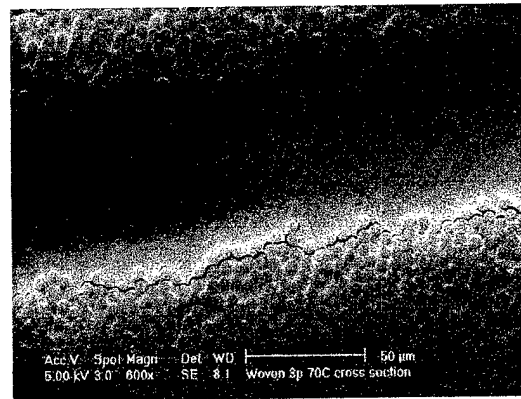
**Fig. 4. Normalized weight gain of 12-ply uni-weave composite and its flash at 70°C.**



**Fig. 5. Normalized weight gain of 3-ply woven composite and its flash at 70°C.**

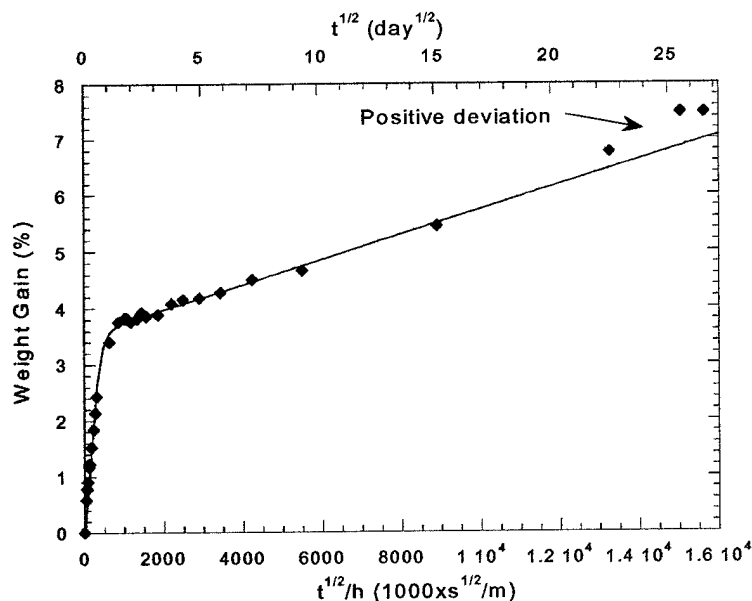


**(a)**



**(b)**

**Fig. 6. SEM micrographs of the cross-section of 3-ply woven composite. (a) After 1 month in 70°C water. (b) After 2 years in 70°C water.**



**Fig. 7. Long-term normalized moisture uptake behavior of 3-ply woven composite at 70°C.**

## **FIBER-MATRIX INTERFACIAL PROPERTIES**

The overall research objective of the AFOSR project is ultimately to improve fiber-matrix interfacial properties of carbon fiber-reinforced bismaleimide (BMI) matrix composites by introducing a LaRC PETI-5 interphase as a high temperature sizing material. Phenylethynyl-terminated imide oligomer (LaRC PETI-5, which is referred to simply as PETI-5 hereafter) used in the present studies has been recently developed at the NASA Langley Research Center. During the last several years, the attraction has grown as a result of the availability of the material. PETI-5 with molecular weight of 2500 g/mol has been shown to possess an excellent combination of processability, high toughness, and mechanical, physical and chemical properties at elevated temperatures. Such favorable combinations of properties make them suitable as potential candidates for coatings, adhesives, films, and composite matrix resins. One possible application under investigation is the use of PETI-5 as a sizing material for carbon fibers and glass fibers for high temperature applications.

To successfully accomplish the objective, the work has been largely divided into three categories as follows: 1) characterization and processing of PETI-5 oligomer and polymer, 2) improved interfacial properties of carbon/BMI composites by an PETI-5 sizing interphase, and 3) the analytical interpretation of the improved interfacial properties in the present fiber/interphase/matrix system. As the consequence, the most work on characterization and processing of the resin to be used as a sizing material has been published in several literatures. The manuscript on the improved interfacial properties is now in preparation for publication. Also, some papers interpreting the



interfacial results will be published in the future. Here we summarize the key results on the basis of the three categories described above.

## 1. Characterization and Processing of PETI-5 Oligomer and Polymer

It is necessary to understand the physical and chemical changes that occur in PETI-5 during solvent removal, imidization, curing and consolidation to optimize resin processing and properties because processing requires the resin to be generally exposed to a prescheduled temperature and time profile. As the very first step of the research work, we studied the changes in molecular structure during reaction through observation of temperature- and time-dependent intensity variations of the characteristic Fourier Transform Infrared (FTIR) absorption bands. From FTIR studies, the imidization and phenylethynyl end-group reaction behavior occurring via thermal imidization and cure of PETI-5 have been extensively interpreted in terms of the disappearance and appearance of several characteristic absorption peaks during dynamic and isothermal heat-treatment. The results gave some information on temperature- and time-dependency of the cure of PETI-5, which may be useful for determining the processing conditions necessary for use as a high-temperature fiber sizing material. The study also measured the extent of imidization and the activation energy of cure reaction of PETI-5.

The research has been extended to thermal characterization of PETI-5 including the glass transition, melting behavior, cure behavior and thermal stability using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results showed that the extent of cure for the partially cured resin was evaluated taking into account the residual NMP solvent in the resin and the thermal history (cumulative, individual, and isothermal cures) for the imidization reaction influences the extent of the cure. The reaction of the C=C bonds in the phenylethynyl groups located in the imide polymer chain ends is completed to produce a fully cured PETI-5 within 1 h at 350°C in air. This study also demonstrated that no reaction takes place above 350°C prior to degradation. The thermal stability of PETI-5 was excellent up to 550°C as long as it is fully imidized. The result of the isothermal stability suggested that this sizing material be used without significant loss of its integrity for extended periods of time below 450°C.

As the next step of the research under cumulative and isothermal heat-treatment conditions have been simultaneously monitored using dynamic mechanical analysis (DMA). This work is to mimic a fiber-interphase-matrix system utilizing a reinforcement of a braided glass fabric substrate sized with PETI-5 amic acid oligomer and to develop suitable sizing process conditions. From the studies, three distinguishable peaks were detected in the  $\tan \delta$  curves, which give useful information on the glass transition temperature ( $T_g$ ), imidization temperature ( $T_i$ ), and cure reaction temperature ( $T_c$ ) together at a time. The degree of imidization or cure reaction occurring during the cumulative and isothermal cure processes is related to the presence and size of the imidization peak and the cure reaction peak. The number and shape of the  $\tan \delta$  peaks also change depending on the given processing temperature. The rate of cure increases substantially above 250°C. The  $T_g$  of the fully cured PETI-5 sized in glass fabric reinforcement strongly depends on thermal history, especially above 300°C.

## **2. Improved Interfacial Properties of Carbon/BMI Composites**

We have studied the interfacial property of IM7 carbon fiber/BMI composites focusing on the interfacial shear strength (IFSS) at the fiber/matrix interface to examine the effect of adhesion enhancement by introducing a PETI-5 interphase sized at different temperatures, 150°C, 250°C and 350°C, using an interfacial testing system (ITS) equipped with a micro-indenter of 5  $\mu$ m tip and a scanning electron microscopy (SEM). BMI with a trade name of Matrimid 5292 was used. The IM7 carbon fiber/BMI composite specimens were prepared in a silicone mold. The results showed that PETI-5 sizing temperature significantly influences the IFSS of IM7 100%/BMI composites processed at full cure conditions. The IFSS of the IM7 100%/BMI composite unsized was largely enhanced by introducing a PETI-5 sizing interphase, especially at a sizing temperature of 150°C. That is, the highest improvement of the IFSS is about 35% in the case of the composite sized at 150°C. The IFSS values decreased with increasing the sizing temperature. The result was also compared with the unsized composites with BMI and PETI-5 matrices, respectively.

The interlaminar shear strength (ILSS) of 2-directional carbon fabric/BMI composite materials fabricated using prepreps unsized and sized with PETI-5 was measured by means of universal testing machine (UTM). The ILSS values of the carbon fabric/BMI composites sized with PETI-5 amic acid oligomer were greater than those of the unsized counterparts. Especially, the composite sized with PETI-5 at 150 showed the highest value of ILSS with an improved interfacial property of about 66%. The ILSS values of the sized composite decreased with increasing sizing temperature. The effect of sizing temperature on the ILSS value obtained by a short beam test exhibited a similar trend with the effect on the IFSS value obtained by an ITS method.

Dynamic mechanical thermal properties of carbon fabric/BMI composites unsized and sized with PETI-5 at 150°C, 250°C and 350°C and a role of the PETI-5 sizing interphase in the composite system were investigated using dynamic mechanical thermal analysis (DMTA). The  $T_g$  values obtained from  $\tan \delta$  peaks of the sized composites were higher than those of the unsized carbon fabric/BMI and carbon fabric/PETI-5 composites. Especially, the carbon fabric/BMI composite sized at 150°C showed the highest storage modulus at 250°C, where imidization has been completed. The result well agreed with the results of IFSS and ILSS of the composites studied earlier. Consequently, it is concluded that the DMTA results in the present work may provide some useful data to understand the effect of PETI-5 sizing interphase on the interfacial property of carbon/BMI composite. The interfacial and dynamic mechanical studies also suggested that a very small amount of PETI-5 applied onto fiber surface significantly influences adhesion properties as well as mechanical behavior of a fiber-reinforced polymer matrix composite.

## **3. Analytical Interpretation of the Improved Interfacial Properties**

The improved interfacial properties in the present carbon fiber/PETI-5/matrix composite system have been analytically interpreted by means of dynamic mechanical

and solid-state fluorescence techniques. Based upon the results from dynamic mechanical and photophysical properties, the reasons for the adhesion enhancement by introducing PETI-5 sized at different temperatures as an interphase to the carbon fiber surface in carbon/BMI composite are successfully explained. It is concluded that there may be some physical interaction like interdiffusion and/or chemical interaction like co-cure occurring at the interfaces between the PETI-5 interphase and BMI matrix in the composite. Sizing temperatures experimentally used in the present studies are 150°C, 250°C and 350°C. It has been found that PETI-5 is partially imidized at 150°C, fully imidized but partially cured at 250°C, and fully cured at 350°C. Among these temperatures, the possibility and frequency of physical interdiffusion may be highest at 150°C. It may have happened that two interdiffused components between BMI and PETI-5 may be chemically co-cured at the interfaces during the sizing process. On the other hand, at 250°C the interdiffusion may be lightly occurred due to fully imidized PETI-5 and at 350°C it may be hardly occurred due to fully cured PETI-5.

To provide experimental evidences such as interdiffusion and/or co-cure, we chose two different molecular systems that may be mimic to the interfaces between the interphase and matrix in a fiber-reinforced polymer composite system. One is an immiscible BMI/PETI-5 blend system, where particulate PETI-5 powder heat-treated at different sizing temperatures is uniformly distributed in uncured BMI matrix. It has been expected from this system that interchangeable penetration probably take place between molecular chains located at the interfaces, depending on heat-treatment temperature. The PETI-5 was heat-treated at 150°C or 250°C varying the addition of PETI-5 to BMI; 5, 10, 20 and 30 wt%. Possible physical changes occurring at the interfaces between BMI and PETI-5 are investigated in terms of dynamic mechanical properties. Based upon tan curves, the T<sub>g</sub> (220-250°C depending on the PETI-5 content) of PETI-5 heat-treated at 150°C was higher than that (205-210°C regardless of the PETI-5 content) heat-treated at 250°C. The T<sub>g</sub> of uncured BMI decreased from 330°C to 310°C with increasing the amount of PETI-5 added to BMI. Below the region of the T<sub>g</sub> of PETI-5, the storage modulus of the blend with PETI-5 heat-treated at 150°C increases with the PETI-5 content. The storage modulus of the blends with PETI-5 heat-treated at 250°C does not depend on the PETI-5 content. The partially imidized PETI-5 is probably easier to be interdiffused or interpenetrated into the uncured BMI resin than fully imidized PETI-5 at 250°C because it may include flexible molecular chains and a small amount of remaining solvent that contributes to increasing the molecular mobility of PETI-5. Conclusively, dynamic mechanical behavior such as tan and storage modulus in immiscible BMI/PETI-5 blends has been interpreted by possible physical interdiffusion at the interfaces between uncured BMI and partially imidized PETI-5 molecules, depending on heat-treatment temperature of PETI-5.

The other molecular system is a double layer one, where each layer is composed of thin film. The top layer is of PETI-5 and the bottom layer is of BMI, or vice versa. We first investigated the variations of the fluorescence spectrum for neat PETI-5 and BMI single layer films, and PETI-5/BMI and BMI/PETI-5 double layer films, respectively. Interestingly, it was observed that there is a remarkable change in the fluorescence spectrum of PETI-5/BMI double layer film in comparison with those of neat

PETI-5 and BMI single layer films, depending on thermal history. The fluorescence spectrum of PETI-5/BMI layer represents the PETI-5 spectrum added by the BMI spectrum, showing an additional red-shift to the right with a maximum around 600 nm. The spectral change and additional red-shift are most pronounced in the double layer films heat-treated at 150°C. Such an additive effect on the fluorescence intensity may indicate that there is a significant physical interdiffusion at the interfaces between PETI-5 and BMI at 150°C. In addition to this, the additional red-shift of the spectrum to higher wavelength probably suggests that some chemical interaction like co-cure may take place at the interfaces between PETI-5 and BMI in the present system. Comparing with the fluorescence results obtained from the specimens heat-treated at 100°C, 180°C and 200°C, the physical and chemical interactions most markedly occur at 150°C, which is a temperature greater than melting point (~120°C) of BMI but lower than primary cure temperature (177°C) of BMI. The fluorescence spectrum depends on isothermal cure temperature. The fluorescence patterns of PETI-5/BMI double layer films heat-treated at 180°C and 200°C indicate that the molecular motion of BMI may be largely restricted to be interdiffused into the top layer of PETI-5 from the bottom layer of BMI. Such physical and chemical behavior at the interfaces was similarly observed in BMI/PETI-5 double layer films but the extent and the temperature dependence are more or less different.

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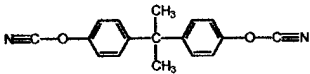
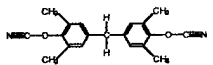
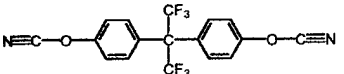
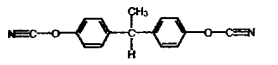
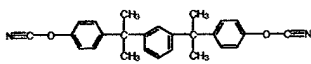
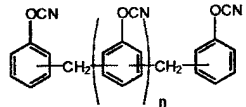
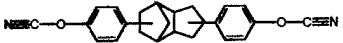
## BMI – CYANATE ESTER BLENDS

### Polymer Blends with Bismaleimides and Cyanate Esters

For some Air Force applications, especially in space structures, cyanate esters and cyanate ester/bismaleimide blends can provide more attractive properties over epoxies and polyimides. These properties include lower moisture uptake and outgassing, lower dielectric constants, resistant to high ionization (up to  $10^9$  rads), and lower viscosity that

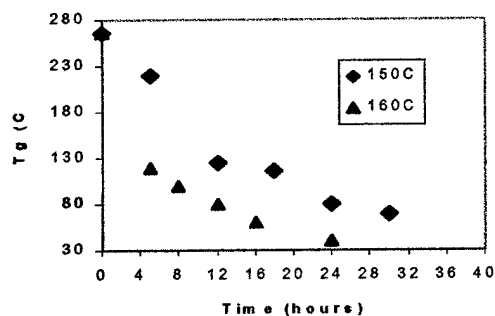
lends to improved processability. There are several commercial cyanate esters, as tabulated in Table I.

**Table I. Some Commercially Available Cyanate Esters**

Structure	Trade name	T <sub>g</sub> (C)	% H <sub>2</sub> O	D <sub>k</sub> @1MHz	G <sub>1c</sub> (J/m <sup>2</sup> )
	AroCy B BT-2000	289	2.5	2.91	140
	AroCy M	252	1.4	2.75	175
	AroCy F	270	1.8	2.66	140
	AroCy L-10	258	2.4	2.98	190
	RTX-366	192	0.7	2.64	210
	Primaset PT REX-371	270- 350	3.8	3.08	60
	XU-71787	244	1.4	2.8	125

However there are some shortcomings for the use of cyanate esters in composite structures, such as relatively low glass transition temperature (250-260°C), susceptibility to steam degradation and brittleness. We examined this degradation by curing samples of bisphenol A-based cyanate ester (AroCy B®) in steel high pressure DSC sample holders, adding a few milligrams of water, sealing the holders and immersing in an oil bath to various times. Glass transition temperatures were measured to measure the extent of

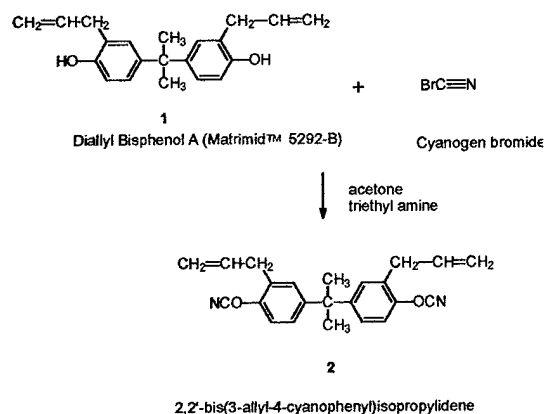
depolymerization. As shown in Figure 1, the cyanurate network is rapidly depolymerized under the steam environment



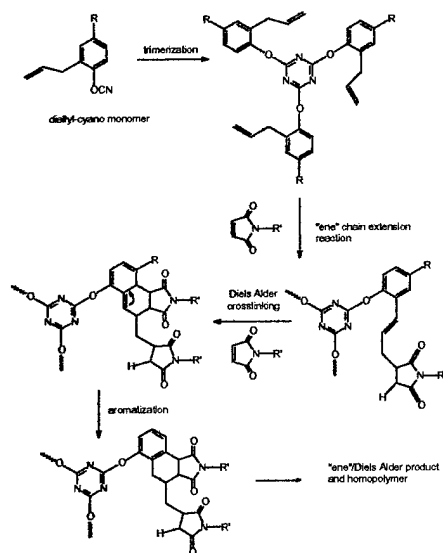
**Figure 1. Glass transition temperature after various hydrolysis times.**

To mitigate some of the shortcomings, the following blends have been explored: (1) with bismaleimides as IPN; (2) with thermoplastics to form 2-phase morphology. However these physical blends do not lead to chemical co-cure, and as such are limited to the properties of the one of the components. One approach to solve this problem is to put functional substituents in the monomers that will co-cure to form a homogeneous polymer network.

By functionalizing one of the components of commercial BMIs, e.g. Matrimid 5292 (Ciba Geigy) with the cyano substituents, it is possible to provide for a chemical linkage between CE and BMI resins. As shown in Figure 2, the modified monomer can be used partially or completely to replace Matrimid 5292B. The anticipated network structure is shown in Figure 3.

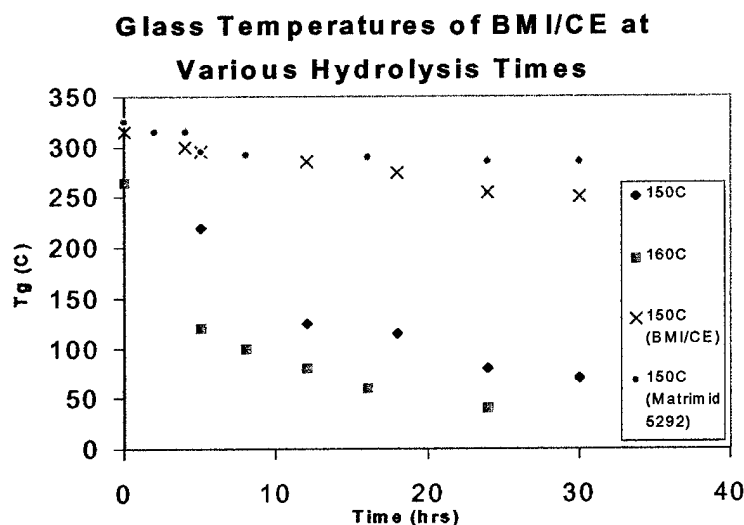


**Figure 2. Synthesis of monomer that co-cures bismaleimides to cyanate esters.**



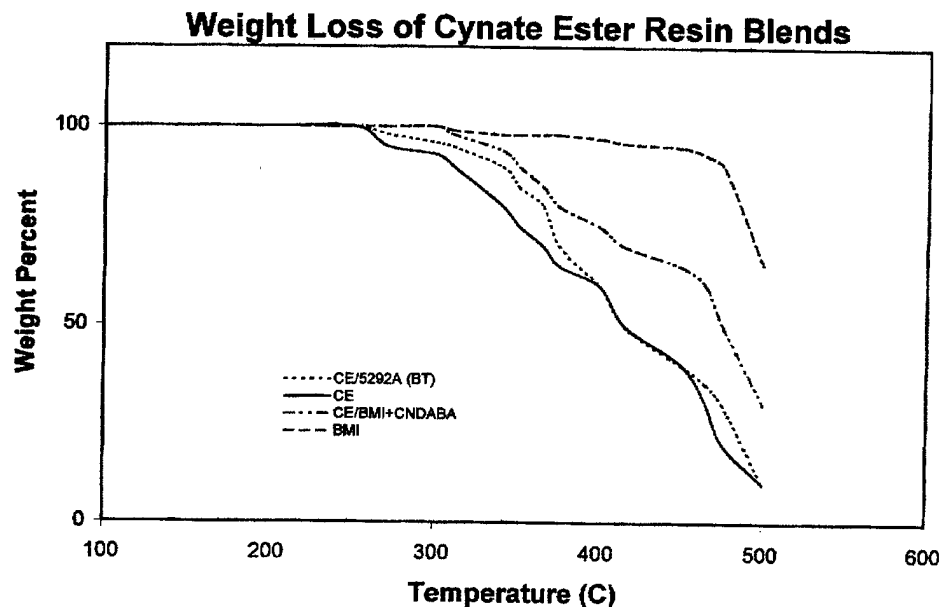
**Figure 3. Reaction mechanism for allyl-substituted cyanate esters and bismaleimides**

By forming chemical linkages between the CE and BMI structures, the hydrolytic stability of the blend is much improved, as shown in Figure 4. This is due to existence of a continuous network even after hydrolytic degradation of the cyanate ester linkages.



**Figure 4. Glass temperature of BMI/CE at various hydrolysis times**

Thermal stability of the polymer blends is also improved over that of the commercial CE/BMI physical blends. As shown in Figure 5, by chemically linking the cyanate ester with reactive sites to the BMI network, the TOS is much improved over that of the commercial physical blend.



**Figure 5. Weight loss of cyanate ester resin blends**

Carbon fiber reinforced composites of the resin blends were fabricated using IM7 fibers and cured according to a typical bismaleimide cure cycle: 2 hours at 177°C followed by a postcure of 2 hours at 200°C and 6 hours at 250°C. Short beam shear strengths were measured at room temperature after various environmental exposure conditions. Table II shows the composite properties of various blends.

**Table II. Short Beam Shear Strengths (in MPa) of Composite Laminates at various exposure conditions**

Test temp (°C)	Exposure Condition	BMI (5292)	CE (ArroCy B)	BT	BMI/CE blend
25	None	117	85	106	115
177	None	82	53	75	79
RT	48h in boiling water	55	20	25	40
25	1000h@230C	110	45	65	107
177	1000h@230C	62	40	45	60



The results indicate that while the blending of bismaleimides into cyanate esters improves the properties of the laminates, the physical blending of cyanate ester and bismaleimide, such as the commercial BT resin, has shortcomings in the hydrothermal stability of the laminate. For significant improvement in the long-term environmental stability of the composite it is highly beneficial to achieve co-curing of the two components by reactive substituents on the monomers.

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## • TASK (2) HYGROTHERMAL INDUCED DAMAGE MECHANISMS OF PI'S AND BMI'S

### • BLISTER FORMATION

When the trapped moisture vapor pressure exceeds the local polymer matrix yield stress during dynamic hygrothermal exposure matrix cavitation will occur, Zheng and Morgan (1). Such matrix cavitation and associated delamination depends on a series of variables such as (i) previous humidity-time-temperature exposure and associated moisture concentration profiles; (ii) component thickness; and (iii) rapid heat-time service environment exposure, such as thermal spikes.

We conducted studies on the blister threshold temperature upon thermal spiking as a function of initial moisture content for a range of P.I.'s and BMI resin (2). The principal findings were:

- BMI's do not blister because cavitation in highly crosslinked thermosets require rupture of numerous covalent bonds.
- Blistering occurs in non-crosslinked or lightly crosslinked P.I.'s with blistering occurring for relatively low initial moisture contents, for example  $\bar{>}$  0.3 to 0.4 wt% moisture content.

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## THERMAL CYCLING/SPIKING

Both dry and moist BMI and PI resins and their carbon fiber composites were thermal spiked from 30°C to 250°C upto 12 cycles (1,2).

Moisture weight gain behavior was monitored during the entire thermal spiking exposure. The exposure cycle consisted of three steps, i.e., (1) initial saturation at 30°C, 90%RH, (2) absorption and desorption during thermal spiking, and (3) desorption during dry conditioning at 80°C in vacuum. Both [0/90] and [0] BMI composite laminates were used to identify the effects of microcracks on moisture absorption behavior. The cross-ply laminate always contained cure-induced microcracks while the unidirectional laminate was completely microcrack-free. At the initial wet conditioning the BMI composite and K3B composite and BMI resin, BMI unidirectional composite, and K3B composite behaved similar, i.e., (i) the moisture content decreased gradually at the early spikes until leveling off at about 50wt% loss and (ii) the amount of water in and out during thermal spiking was about 30-40% of maximum moisture content. On the other hand, both cross-ply BMI composites the microcracks are the main cause of the high diffusivity while the intergranular boundary effect is suspected for K3B resin since the resin plaque was fabricated by compression molding of a fully imidized K3B powder. It was also observed that the diffusivity of the K3B composites was almost doubled after the spiking exposure because of the hygrothermal-induced damage; micro-cavitation, blistering and delamination. Interestingly enough, there are always some residual moisture left in all BMI/IM7 composite regardless of drying time while BMI resin, K3B resin and composites came back to the original dry weight. This is most likely due to that the wet Tg of the BMI composites is higher than the spiking temperature so that some lock-in moisture can not diffuse out at lower drying temperature.

Residual mechanical property changes before and after thermal spike exposure were monitored. No significant property modification was detected.

Thermal cycling, upto 8 cycles, under moist and dry conditions between 23°C and 80°C were completed for BMI and PI – carbon fiber composites. Again, no significant mechanical or thermal property deterioration was detected (1).

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## MOISTURE "LOCK-IN"

The issue of small quantities of absorbed moisture in the 0.2 – 0.4 wt% range, that can cause blistering upon aerodynamic simulated thermal spike exposure, being molecularly "locked-in" the resin was continued to be studied (1,2).

An accelerated hygrothermal aging experiment followed by a systematic drying program as a function of time and temperature was performed on P.I. resins. It was concluded that water molecules locked into the molecular structure at high temperatures can only diffuse out upon subsequent exposure to same high temperatures. The "locked-in" moisture was in the 0.1 to 0.4 wt% range.

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## HYDROLYTIC DEGRADATION

Polyimides are susceptible to hydrolytic polymer chain scission as a result of (i) scission of any inherent amide group defects present as a result of non-ring closure to the imide ring and (ii) imide ring opening to amide formation followed by scission of the amide group. Hydrolytic attack of the imide ring reverses the polymerization reaction, resulting in the formation of the polyamic acid, followed by chain scission and associated molecular weight and strength decreases resulting ultimately in regeneration of the monomers (1).

The geometric position of the hydrolytic induced scission in a thermoplastic polymer chain or in a thermoset crosslinked network can significantly effect the resulting mechanical strength decrease.

For the thermoplastics, one random scission per macromolecule, which is a scission of <1% of the total inherent initial imide rings causes the strength to decrease by ~50% (2). However, if hydrolytic attack preferentially occurs at the ends of the macromolecules, as we have observed for Kevlar, polyphenylene terephthalamide, macromolecules that results in acid or amine monomer formation (3), there is no direct initial strength decrease. The acid monomer can however, catalyze hydrolytic random chain scission because acids can accelerate imide and hydrolyses by up to  $\sim 10^5$  times faster (1,2).

For thermosets, hydrolytic scission at a crosslink rather than in an inter-crosslink network segment would cause more serious mechanical property deterioration because crosslink scission which generates 1.5. to 2 greater the number of disconnected network defects, depending if the crosslink has 3 or 4 network interconnections.

In order to ascertain the characteristics and kinetics of hydrolytic degradation of PI's where <1% scissions can cause a ~50% decrease in strength requires:

- Accelerated test procedures at high temperatures (177 – 250°C); and
- Monitoring thermoplastic molecular weight ( $M_n$ ) changes of  $\leq 100$  m diameter PI powders by sensitive gel permeation chromatography, GPC, after exposure to moist environments at  $\leq 100^\circ\text{C}$ . (Fine,  $\leq 100$  m PI powders allow complete exposure of the PI to the moisture). Other measurement techniques such as FTIR of imide ring concentrations: DSC of Tg's and monomer melting points; and strength measurements were used to compliment the above test procedures.

For the accelerated high temperature hygrothermal exposures of PI powders in a pressure bomb, care was taken during exposure and cool down that the powders only ever are exposed to moisture vapor which directly simulates diffusion and mobility of water molecules moving from one polymer H-bond to another within the polymer.

The principal findings for accelerated hygrothermal testing of K3B, AFR700B and PETI-5 PI's in the 200-250°C as a function of exposure time in days.

For K3B PI at 250°C after one day hygrothermal exposure, the Tg completely disappeared in a DSC run to 400°C. The second DSC run shows the reversibility of the degradation with the reappearance of the Tg 20°C below the initial Tg. For longer time exposures up to 8 days FTIR shows the complete disappearance of the imide groups. After 200°C hygrothermal exposure, DSC exhibits two distinct endothermic melting points at 160° and 270°C associated with inherent amine and acid monomers respectively. The progressive decrease in intensity of the acid melting point peak indicates slow decarboxylation of the acid that will thus inhibit complete polymerization reversibility. After subsequent exposure to 400°C, after 200°C hygrothermal exposure, we observed near complete recovery of the inherent imide groups by FTIR. The mechanical strength of K3B deteriorates by ~95% after one day hygrothermal exposure at 200°C, with <10°C Tg decrease, but we observed only by ~5% decrease in strength after 1,000 hours exposure at 160°C and no Tg decrease.

AFR700B PI strength deteriorates much more rapidly than K3B PI after 1,000 hours hygrothermal exposure at 160°C exhibiting a ~70% decrease, together with a 75°C Tg decrease. Such "lower" temperature hygrothermal-induced property deterioration is associated with hydrolytic chain scission of the norbornene based crosslinks in AFR700B PI.

PETI-5 PI, from initial hygrothermal degradation exposure studies at 250°C, exhibits significantly more degradation resistance than K3B PI with a 50°C decrease of the Tg after eight days exposure, whereas for K3B PI the Tg is completely eliminated after similar exposure conditions. Note PETI-5, because it is crosslinked through ethynyl terminated end groups contains no acid or amine chain ends which are present in K3B PI.

The observed hydrolytically-induced formation of acid and amine monomers from these end groups in K3B PI can result in products that catalyze further hydrolytic degradation.

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## • TASK (3) ACCELERATED SYNERGISTIC TESTING

A synergistic durability test facility was developed that was capable of monitoring the combined effects of:

- Thermal cycling from upto 400°C down to cryogenic temperatures;
- Isothermal time exposure;
- Stress; and
- Flowing surface gas exposure of variable composition and flux; upon composite surface microcrack initiation and propagation (1-3). This facility was capable of simulating a range of composite aero-propulsion service environment conditions.

The facility was utilized to study the effects of gas composition on the surface thermo-oxidative degradation of PI-carbon fiber composites, specifically with the addition steam environments compared to dry air. It was demonstrated that the addition of steam accelerated surface "corrosion" rates as a result of hydrolytic degradation of the PI resin.

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#### • TASK (4) PI COMPOSITE/RESIN STRUCTURE-PROPERTY RELATIONS

Thermal-processing structure-property relationships for polyetherimide (PEI), poly (4, 4 - oxydiphenylene pyromellitimide) (POPPI), and phenylethynyl-terminated imide (PETI-5) composite matrices were studied from a fundamental perspective (1,2).

For thermoplastic PEI, deformation and failure depend primarily on free volume as evidenced by moisture-absorption, mechanical-property, and mass-density changes as a function of annealing. The deformation of POPPI can be divided into the following three regimes as a function of annealing temperature: (1) physical aging-induced glassy state free-volume decreases, (2) thermally activated microvoid collapse, and (3) chemical degradation. In the case of PETI-5, macroscopic defects, free volume, and polymer morphology control deformation. The effects of residual crystallinity on deformation are reported, and it is shown that mechanical toughness can be significantly decreased upon annealing below the glass-transition temperature.

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